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# EXPLORING THE CONSEQUENCES OF NEGATIVE TRIPLE JUNCTION ENERGY

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## ABSTRACT
We have investigated the consequences of negative triple junction energy in grain growth. Two and three-dimensional models for total system energy, incorporating varying triple junction energy are developed. These models show that there is a decrease in overall system energy with grain size corresponding to the driving force for grain growth. Although the free energy available to drive grain growth is reduced under some conditions, it is never removed for any reasonable values of the triple junction energy.

## INTRODUCTION
Ultrafine-grained materials are characterized by a very high density of grain boundaries. Palumbo and Aust [1] have pointed out that in the nanometer grain size regime, the density of triple junctions also becomes a potentially important consideration, with the volume of triple junction material exceeding the volume of grain boundary material at a grain size of about 3 nanometers. If triple junctions have properties that differ from those of the grain boundaries [2] then they may exert a powerful influence upon materials behavior in nanostructured materials.
Srinivasan, Cahn and Kalonji [3] have suggested that triple junctions may have "negative" energy and this would certainly be expected to result in unusual behaviors wherever there is a large concentration of triple junctions in a material. In fact, "negative" triple junction energy corresponds to an energy that is lower than that of the adjacent grain boundaries, but is still greater than the energy of the corresponding crystalline material. Even with this understanding, its existence remains somewhat controversial [4].
The purpose of this paper is to investigate the possible effects of reduced triple junction energy on the overall driving force for grain growth, to see if it can contribute to the stabilization of ultrafine microstructures. At its most basic level, the driving force for grain growth is the reduction of interfacial energy that accompanies increasing grain size, and we compute this overall interfacial energy taking account of grain boundaries, triple junctions and quadruple points as potentially different components of the microstructure. The computations are performed for model microstructures corresponding to columnar-grained thin films, and equiaxed bulk polycrystals.

## 2-D MODEL
We consider a microstructure comprising uniformly sized regular, hexagonal grains with edge length '$a$' and a grain boundary thickness '$\delta$'. The grain boundaries (GBs) are rectangular slabs and the triple junctions (TJ's) are equilateral triangular prisms as shown in Fig.1. There are no quadruple points. The energy of the system depends on the amounts of the various features present in it, which vary with the grain size. Fig.2 shows a plot of the cumulative volume fractions of the various features with varying equivalent cylindrical grain diameter. Assigning reasonable

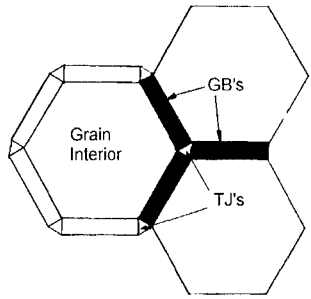


**Fig.1**: Regular hexagonal grains showing GB's and TJ's.

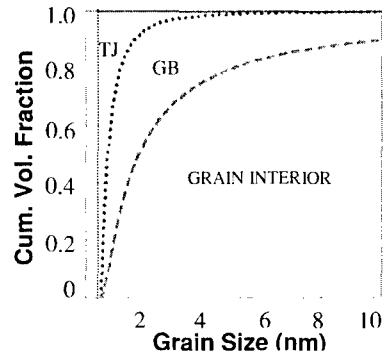


**Fig.2**: Cumulative volume fractions of different components as a function of the grain size, for a GB thickness=0.5nm, for the 2-D model. At a grain size of 2nm, the solid comprises of 54.4% Grain Interiors, an additional 38.7% of GB material, and 6.8% of TJ material.

values to the GB and TJ energies we examine the behavior of the system energy. No variation of energy among the GBs or the TJs is considered, *i.e.* we adopt a "uniform boundary" model, and we assume that no interaction energies exist among the various defects in the system, so the energies of the individual components can be straightforwardly summed. The energies assigned to the defects were:

GB energy = 1 $J/m^2$, corresponding to an energy density of $1/\delta$ $J/m^3$
TJ energy density varying between 90% and 10% of the GB energy density.

corresponding to a range of modest through extreme cases of "negative" TJ energy. These are all excess Gibbs free energies associated with the defects. The energy of the grain interior is the ground state for the system, and is arbitrarily set to zero. Fig.3 shows the corresponding system energy as function of the grain size, in the nanometer range. In order to account for the possibility that the grain boundary structure (and hence energy) also varies with grain size [5] we have investigated a model in which the GB width varies inversely with grain size. For modeling purposes we choose the following variation:

| | |
|---|---|
| $\delta = 1$nm | for $d \leq 1$nm |
| $\delta = (9.5 - 0.5d)/9$ | for $1 \leq d \leq 10$nm |
| $\delta = 0.5$nm | for $d \geq 10$nm |

The results for the above variation are shown in Figs.4 and 5.

## 3-D MODEL

As a model three-dimensional case we adopt a structure comprising regular Tetrakaidecahedron-shaped (TKD) grains with edge length '*a*' and GB thickness $\delta$ as shown in Fig.6. The TKD is a 14-sided figure with 8 hexagonal and 6 square sides, that is frequently used as an approximant

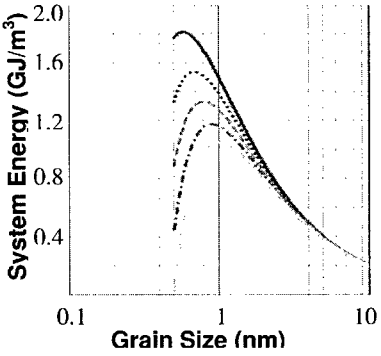


**Fig.3**: Variation of system energy with grain size, for GB thickness=0.5nm, for the 2-D model.

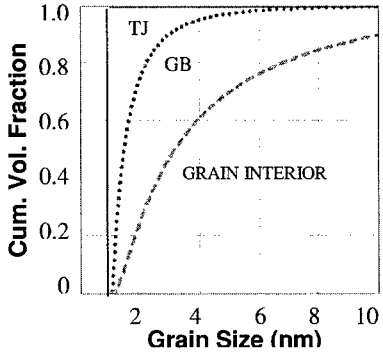


**Fig.4**: Variation of cumulative volume fraction with grain size, for variable GB thickness, for the 2-D model.

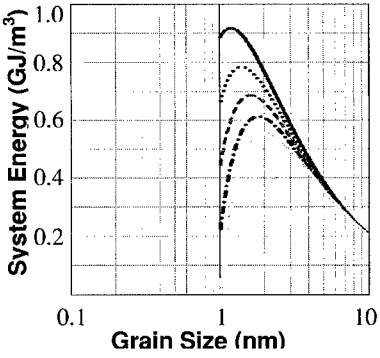


**Fig.5**: Variation of system energy with grain size, for variable GB thickness, for the 2-D model.

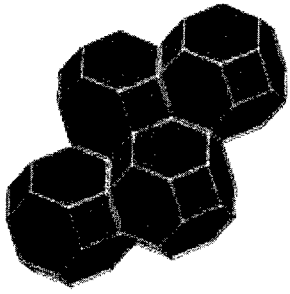

**Fig.6**: A few TKD's stacked in space.

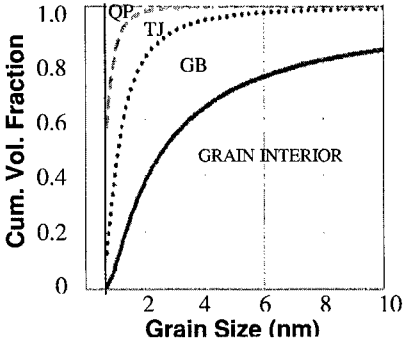


**Fig.7**: Variation of cumulative volume fraction with grain size, GB thickness=0.5nm, for the 3-D model.

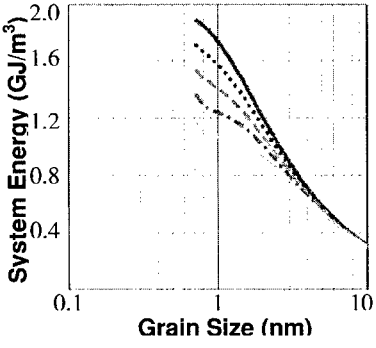


**Fig.8**: Variation of system energy with grain size, for GB thickness=0.5nm, for the 3-D model. QPE=GBE.

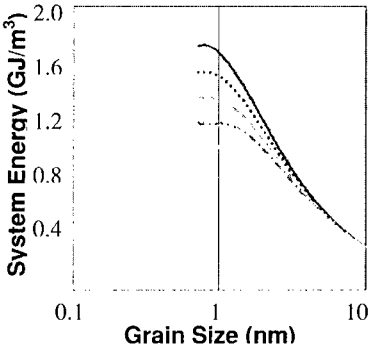


**Fig.9**: Variation of system energy with grain size for GB thickness=0.5nm, for the 3-D model. QPE=80%GBE.

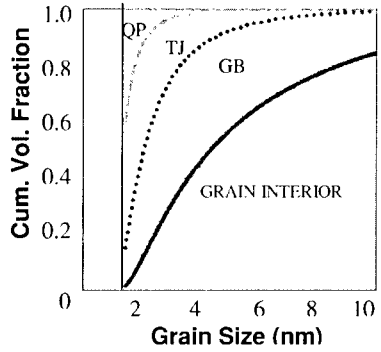


**Fig.10**: Variation of cumulative volume fraction with grain size, with varying GB thickness, for the 3-D model. The variation of GB thickness, to model varying GB properties at small grain size, is described in the text

to the shape of a three-dimensional grain, because it can fill space without leaving any voids and it preserves the topology and proper connectivity of all significant features (GBs, TJs and QPs). For any fixed grain boundary thickness, the triple junctions are polyhedra with uniform, isosceles triangular cross section (since the sides of the TKD do not meet at 120°). The quadruple points (QPs) are tetrahedra with four equal faces in the shape of isosceles triangles. The grain interior becomes an irregular TKD when the interfacial thickness is considered. The cumulative volume fractions of the various features vary with grain size, as shown in Fig.7. Assigning reasonable values to the QP, TJ and GB energies we can study the variation of the system energy with grain size, which is characterized as the equivalent sphere diameter. The energy values chosen are:

| | | | |
|---|---|---|---|
| Case 1: | GB: 1J/m$^2$; | [TJ]: 90% - 10% [GB]; | [QP] = [GB] |
| Case 2: | GB: 1J/m$^2$; | [TJ]: 90% - 10% [GB]; | [QP] = 80%[GB] |

Where [xx] = Energy density. Figs. 8 and 9 show the corresponding system energy as a function of the grain size, in the nanometer range. Now we vary the GB width with grain size in a fashion similar to that done in the 2-D model, and see how the volume fractions and the system energy change. The results for the above variation are shown in Figs.10, 11and 12.

## DISCUSSION

In our models, the volume fractions of the various features (grain interiors, GBs, TJs) are calculated as a function of the grain size, using simple geometry, and elementary simplifying assumptions. Any possible effect of grain size on grain boundary structure or energy is included by allowing the grain boundary width to vary at the smallest grain diameters. Interfacial material is an increasingly dominant fraction of the solid volume as grain size decreases, and at extremely small grain sizes, the grain junctions (TJs and QPs) can occupy as much volume as the grain boundaries themselves.

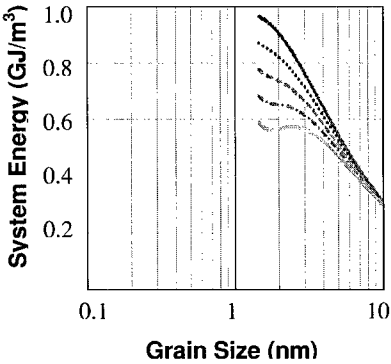


**Fig.11**: Variation of system energy with grain size, for variable GB thickness, for the 3-D model. QPE=GBE

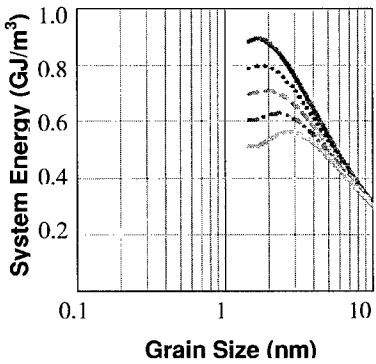


**Fig.12**: Variation of system energy with grain size for variable GB thickness, for the 3-D model. QPE=80%GBE.

A negative derivative of the system energy with respect to grain size represents the global driving force for grain growth, although local topological effects are not considered in this model. In a few of our calculations we find cases where the curve has a minimum and the derivative becomes positive over some range of grain sizes. The energy minimum would correspond to a stable grain size, in the absence of any local topological effects. All minima discovered in this work, however, occur for extreme cases of negative TJ energy, and at unphysically small grain sizes, for which the volume of grain interior material is smaller than the volume of interfacial material. Based on the observed variability of TJ properties [6], we believe that it is extremely unlikely that all of the TJs in the polycrystal would have the same energy, and it is even more unlikely that it would be as low as necessary to stabilize the microstructure, on the basis of the removal of driving force alone. At the most, "negative" TJ energy might be expected to slow grain growth at nanocrystalline grain sizes, relative to the expected high rates, but it does not provide a mechanism for halting it. Observations of reduced grain growth rates have been reported for nanocrystalline Fe [7] but the effect is maximized at a grain diameter somewhere between 20 and 30nm – about an order of magnitude greater than the grain size at which any effect of "negative" TJ energy could be expected. Although varying grain boundary width can move the energy minimum to slightly higher grain sizes, it is doubtful that any systematic change of grain boundary properties with grain size would allow it to reach 20nm, for any reasonable value of TJ energy. We believe that the observed retardation of grain growth is due to impurity-induced pinning, or triple-junction drag [8].

A curious, and possibly unphysical feature of our computations occurs at extremely small grain sizes – typically below one nanometer, depending on the exact choice of TJ energy. At these grain sizes, the TJ volume fraction is comparable to the GB volume fraction and the increasing volume of low-energy TJ material, as grain size shrinks, produces a positive derivative of energy with respect to grain size. This corresponds to a global driving force for grain *shrinkage*, below some critical grain size. If grain shrinkage really does occur, then the result might be the spontaneous amorphization of the material, once the grain size is reduced below the critical, metastable value. Amorphization of various materials has been achieved by ball milling, which first reduces the

grain size [9, 10]. Models for this effect based upon strain energy accumulation [9] could easily be re-cast as effects of strain energy on the relative energies of the intercrystalline components.

## CONCLUSIONS

At ultrafine grain sizes the volume fraction of the intercrystalline region becomes dominant and as the grain size decreases into the nanometer scale, TJ's and QP's account for an increasing fraction of the Intercrystalline region and of the overall microstructure. The negative slope of the total system energy with respect to grain size represents the global driving force for grain growth. It is possible for the system energy to exhibit minima, representing locally stable microstructures, for certain energy configurations. However, the grain sizes in question are unphysically small and carry no significance. "Negative" junction energy on its own cannot be responsible for microstructural stabilization.

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